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(54) [ Title of the Invention ] Polymer electrolyte film and production thereof  
(57) [ Abstract ]

[ Constitution ] A polymer electrolyte film, comprising a porous polymer film produced by stretching, and an ion exchange resin present at least within the pores of said porous film.

[ Effects ] Prevents rupture of the polymer electrolyte film due to expansion and contraction of the ion exchange resin occurring during operation of the unit in which the



polymer electrolyte film is installed, thereby prolonging the life of the polymer electrolyte film and thus extending the life of a solid polymer fuel cell or water electrolysis unit in which it is installed.

[ Claims ]

[ Claim 1 ] A polymer electrolyte film, comprising a porous polymer film produced by stretching, and an ion exchange resin present at least within the pores of said porous film.

[ Claim 2 ] A method for producing a polymer electrolyte film, characterized in that a porous polymer film produced by stretching is impregnated with a solution of an ion exchange resin, followed by removal of the solvent.

[ Detailed Description of the Invention ]

[ 0001 ]

[ Field of Industrial Utilization ] The present invention relates to a polymer electrolyte film for use in solid polymer fuel cells, water electrolysis units, and the like, [and particularly to] a polymer electrolyte film that does not experience rupture with repeated deformation occurring under the operating conditions of the unit; and to a production method for such a film.

[ 0002 ]

[ Prior Art ] Demand is growing for improved energy efficiency on the part of polymer electrolyte films for use in solid polymer fuel cells, water electrolysis units, and the like. This necessitates reductions in the film resistance of polymer electrolyte films, to which end attempts are being made to reduce film thickness. However, thinner films inevitably have lower strength, making the electrolyte film susceptible to rupture when installed in a solid polymer fuel cell or water electrolysis unit, to splitting due to the pressure differential across the installed film, or to cracking of seal portions situated about the periphery of the film.

[ 0003 ] To prevent such damage, Examined Patent Publication (Kokoku) 1-57693 proposes a method of embedding an ion exchange resin in woven fabric by way of a polymer electrolyte film and production method therefor.

[ 0004 ]

[ Problems Which the Invention Attempts to Solve ] Polymer electrolyte films employing conventional reinforcing materials such as woven fabric can experience peeling at the woven fabric fiber-ion exchange resin interface, resulting in shedding of the ion exchange resin so as to leave holes in the polymer electrolyte film.

[ 0005 ] A possible cause of this phenomenon is as follows. Changes in the water content of the ion exchange resin cause it to expand and contract. The woven fabric used

as the reinforcing material for the polymer electrolyte film, on the other hand, acts to constrain expansion and contraction of the ion exchange resin, thereby creating stress at the woven fabric fiber-ion exchange resin interface. Accordingly, in devices wherein operating conditions (e.g. output) fluctuate cyclically, such as a water electrolysis unit or solid polymer fuel cell, the repeated stress will eventually result in separation at the interface.

[ 0006 ]

{ Means Used to Solve the Problems ] The inventors perfected the invention as a result of extensive research directed towards a polymer electrolyte film that would not rupture despite cyclical fluctuations in the water content of the ion exchange resin. The invention resides in a polymer electrolyte film comprising a porous polymer film produced by stretching, and an ion exchange resin present at least within the pores of said porous film; and in a method for producing a polymer electrolyte film characterized in that a porous polymer film produced by stretching is impregnated with a solution of an ion exchange resin, followed by removal of the solvent.

[ 0007 ] The porous polymer film used in the invention may be produced in the following manner. A fluororesin (e.g., polytetrafluoroethylene, etc.) or other resin (e.g., polypropylene, polyethylene, etc.) is subjected to stretching along at least one axis at a temperature below the crystal melting point of the material, and then in the stretched state to heating to above the crystal melting point of the material, as taught in Unexamined Patent Application (Kokai) 42-13560 and Unexamined Patent Application (Kokai) 51-18991, to produce the three-dimensional network structure polymer porous [film] used in the invention. Preferred thickness for the porous film used in the polymer electrolyte film of the invention is from 10 to 200  $\mu\text{m}$ , preferred mean pore size is from 0.1 to 10  $\mu\text{m}$ , and preferred void content is from 50 to 95%.

[ 0008 ]

[ Operation of the Invention ] Where a polymer electrolyte film comprises a porous polymer film produced by stretching, and an ion exchange resin present at least within the pores of this porous film, rupture of the polymer electrolyte film due to cyclically fluctuating operating conditions during operation of a device can be prevented. While the reasons for this are not fully understood, the following hypothesis is possible.

[ 0009 ] Since a porous polymer film produced by stretching has a three-dimensional network structure, it can stretch and contract in any direction. Accordingly, polymer electrolyte films comprising porous polymer film produced by stretching and an ion exchange resin present at least within the pores of the porous film can stretch and contract in association with expansion and contraction of the ion exchange resin, rendering the

material resistant to separation at the ion exchange resin-porous polymer film interface and preventing rupture of the polymer electrolyte film.

[ 0010 ] The use of a porous film produced by biaxial stretching affords a more developed three-dimensional network structure, as a result of which polymer electrolyte films comprising porous polymer film produced by biaxial stretching and an ion exchange resin present at least within the pores of the porous film can stretch and contract appreciably in association with expansion and contraction of the ion exchange resin, rendering the material even more resistant to separation at the ion exchange resin-porous polymer film interface and enhancing the effect of preventing rupture of the polymer electrolyte film.

[ 0011 ] The polymer electrolyte film of the invention will in preferred practice be prepared by impregnating a porous polymer film with a solution of an ion exchange resin and then drying to anchor the ion exchange resin to the porous polymer film. The solvent may be selected with reference to the type of ion exchange resin; for the perfluorocarbonsulfonic acid used in the Example, for instance, isopropanol or other such solvent is preferred.

[ 0012 ] The ion exchange resin concentration in the solvent is typically from 1 to 5%. Excessively low concentrations will necessitate repeated impregnation and drying processes in order to impregnate the porous polymer film with the required amount of the ion exchange resin, while excessively high concentrations will result in high solution viscosity, making for a difficult impregnation process or resulting insufficient penetration of the solution into the porous film.

[ 0013 ] Drying temperature is likewise selected as appropriate for the type of solvent being used. Drying may be conducted in partial vacuum where needed.

[ 0014 ] When dry, the ion exchange resin content of the porous polymer film is from 1 to 100 g per 1 g of porous film, and preferably from 10 to 40 g.

[ 0015 ]

[ Examples ]

Example 1

(I) A porous film of stretched polytetrafluoroethylene (mean pore size 1  $\mu$ m; thickness 50  $\mu$ m; porosity 90%) was impregnated with a 5 wt% isopropyl alcohol solution (ex Aldrich Chemical) of perfluorocarbonsulfonic acid (NAFION ex DuPont) and dried at 60°C. (II) The film was subjected to heat treatment for 5 minutes at 140°C. Processes (I) and (II) were repeated until pinholes were no longer observed (five cycles).

[ 0016 ] The film was then immersed for one hour in 1 N sulfuric acid at 60-70°C and then immersed for one hour in purified water at 60-70°C, to effect substitution of the end groups of the ion exchange resin chains with  $-\text{SO}_3\text{H}$  [moieties].

[ 0017 ] Comparative Example 1

A 25-mesh doup weave composed of a 200-denier polytetrafluoroethylene multifilament weft and a 200-denier polytetrafluoroethylene multifilament warp was selected as the As woven reinforcing fabric. The woven reinforcing fabric was (I) impregnated with 5 wt% NAFION solution (ex Aldrich Chemical), dried at 60°C, and then (II) subjected to heat treatment for 5 minutes at 140°C. Until pinholes were no longer observed, processes (I) and (II) were repeated (five cycles) until film thickness of 50  $\mu\text{m}$  was reached. No pinholes were noted.

[ 0018 ] The film was then immersed for one hour in 1 N sulfuric acid at 60-70°C and then immersed for one hour in purified water at 60-70°C, to effect substitution of the end groups of the ion exchange resin chains with  $-\text{SO}_3\text{H}$  [moieties].

[0019] The films prepared in Example 1 and Comparative Example were subjected to an "expansion cycle test." After the test, while no pinholes were noted in [the film of] Example 1, pinholes occurred over 20% of the film of Comparative Example 1.

[ 0020 ] The "expansion cycle test" was conducted as follows. The polymer electrolyte film was cut into a disk 6 cm in diameter, and a O-ring was arranged on the peripheral area (5-cm diameter) thereof, sandwiched from above by a presser element of donut configuration. The presser element was secured in place at six locations with nuts and bolts, and [the assembly] was immersed in 90°C purified water for 5 minutes, removed, and then dried for 5 minutes at 100°C. This immersion/drying process was repeated for 10 cycles, after which time the films were examined visually for holes produced by shedding of the ion exchange resin. Examinations was also made of air leaks through the film created when one side of the film was pressurized, and of pinholes.

[0021]

[ Effects of the Invention ] The polymer electrolyte film of the invention is effective in preventing rupture of the polymer electrolyte film with repeated expansion and contraction of the ion exchange resin occurring during operation of the unit in which the polymer electrolyte film is installed, and is therefore advantageous for use in fields such as solid polymer fuel cells and water electrolysis units.